

## **FIXED ABRASIVE TOOLS AND ASSOCIATED METHODS**

### **FIELD OF THE INVENTION**

5 The present invention relates to devices and methods for use in connection with polishing various workpieces. More particularly, the present invention relates to polishing tools which incorporate nanodiamond, and accompanying methods for making and design thereof. Accordingly, the present invention involves the fields of chemistry, metallurgy, and materials science.

### **BACKGROUND OF THE INVENTION**

10 In various industrial applications, it is often desirable to polish a workpiece to obtain a quality finish having a low surface roughness. Chemical mechanical planarization (CMP) has become a widely used technique for removing material from a workpiece. In particular, CMP is particularly useful for polishing expensive workpieces including ceramics (e.g.,  
15 sapphire), silicon (e.g., wafers, semiconductor devices, etc.), GaAs (e.g., diodes), GaN (e.g., LED), glass (e.g., LCD), quartz (e.g., oscillators), gemstones (e.g., diamond, ruby, cubic zirconia, etc.), metals (e.g., refractory metals or precious metals such as platinum), combinations of these materials for use in semiconductors, electro-optical devices, reflectors, jewelry, and the like. Generally, the polishing process entails applying a wafer  
20 against a flat horizontally-rotating pad, often porous or fibrous, made from a durable organic substance such as polyurethane. To the rotating pad, is added a slurry containing a chemical solution and abrasive particles. The chemical solution is capable of chemically reacting with the wafer constituents (e.g., copper circuitry or other features) to form easily removable chemical species (e.g., copper oxides). In addition, abrasive particles help the  
25 pad to physically polish the wafer surface and remove reactants from the surface. The slurry is continually added to the spinning CMP pad, and the combined chemical and mechanical forces exerted on the wafer cause it to be polished in a desired manner. Such polishing processes can be effective, but also suffer from sensitive control parameters and large volumes of abrasive slurry waste.

During the course of polishing, the pores or fibers of the CMP pad become clogged with debris removed from the workpiece or the pad, as well as abrasive particles from the slurry trapped along with the debris. Moreover, the pad fibers can be subjected to high temperatures during contact with the wafer surface. As a result, irreversible changes can occur due to partial melting of the pad. Further, accumulation of debris and abrasive particles can cause glazing or hardening of the pad. This accumulation within the pad fibers reduces its capacity to store slurry and support abrasives for effectively removing material from the workpiece. Therefore, a CMP pad of this type is typically "dressed" or "conditioned" using a CMP pad dresser or conditioner. A variety of such conditioners, including specific methods for the use and manufacture thereof, are known in the art.

While pads utilizing a slurry have been effective in achieving a wide variety of polishing results, such pads suffer various drawbacks such as abrasive particle aggregation. Particularly, due to the centrifugal force of the horizontally spinning CMP pad, the loose abrasive particles from the slurry tend to group, or gather, in the more shallow regions of the pad. Thus, when used to polish certain materials, such as softer metals, uneven depressions known as "dishing" can occur. Additionally, because the abrasive particles are not physically attached to the pad, but rather are free moving, it is difficult to increase the rate of material removal from a workpiece by simply increasing the rotation speed of the pad.

In order to solve these and other problems, CMP pads which include abrasive particles that are embedded in, or otherwise fixed to, the pad, rather than provided in a slurry, have become known in the art, such as those disclosed in U.S. Patent Nos. 5,453,312; 5,454,844; 5,692,950; 5,820,450; and 5,958,794, each of which is incorporated herein by reference. A chemical solution is still typically used with such fixed abrasive pads. However, because the abrasives are embedded in the pad, a slurry which contains abrasive particles is not needed. Additionally, the polishing surface of a fixed abrasive pad contains a plurality of small projections known as "poles." Typically, because the poles may be manufactured to a uniform height above the polishing surface, fixed abrasive CMP pads are capable of achieving a superior flat surface on a workpiece as compared to conventional CMP pads.

Unfortunately, most fixed abrasive polishing pads result in excessive scratching of polished surfaces. Typical abrasives used in these fixed abrasive pads are either too large and/or contain excessive sharp edges which do not allow for ultra-fine polishing and leave excessive scratches on the workpiece. This excessive scratching is generally unacceptable for applications where a high degree of smoothness is required. As such, devices and methods for improved fixed abrasive tools and methods of producing them continue to be sought.

### **SUMMARY OF THE INVENTION**

Accordingly, the present invention provides a fixed abrasive tool suitable for polishing a workpiece. In one aspect, the fixed abrasive tool can include a polishing layer on a substrate. The polishing layer can include an organic matrix with nanodiamond particles therein. The polishing layer can be formed in a wide variety of configurations, depending on the specific polishing application. Most often, the polishing layer can include a plurality of projections.

Various aspects of the projections, such as height, width, geometric shape, and organization, can be varied in order to achieve a particular result. For example, in one aspect, the projections can take a wide variety of geometric shapes, including without limitation, conical, frustoconical, pyramidal, frustopyramidal, cubic, parallelepiped, rectangular, cross, cylindrical, column, ridge, and combinations thereof. Similarly, the arrangement of projections can be such that the fixed abrasive tool has a loading ratio of from about 0.05 to about 0.5.

Nanodiamond particles used in the present invention typically can have a particle size from about 1 nm to about 50 nm, and preferably about 2 nm to about 10 nm. In one specific aspect, the nanodiamond particles can include a carbonaceous coating. This carbonaceous coating can provide beneficial lubrication effects, without substantially reducing removal of material from a workpiece. Most often, the carbonaceous coating includes a thin layer of non-diamond carbon, e.g., fullerenes, surrounding each nanodiamond particle.

The principles of the present invention can be used to form a variety of fixed abrasive tools. For example, in one preferred aspect, the fixed abrasive tool can be a CMP polishing pad.

5 The present invention additionally encompasses methods for making the fixed abrasive tools as disclosed herein. According to one embodiment, a method of making a fixed abrasive tool includes the steps of providing a suitable substrate and preparing a slurry comprising nanodiamond particles and an organic binder. Such a method can further include the step of forming the slurry on the substrate in a predetermined three-dimensional pattern. The slurry can then be solidified to produce abrasive projections including an  
10 organic matrix and nanodiamond particles.

In one detailed aspect of the present invention, the slurry can be screen printed on the substrate. Additionally, several layers of slurry can be screen printed to form a variety of predetermined three-dimensional patterns. Alternatively, the slurry can be tape cast to form a polishing layer. In such embodiments, portions of the tape cast slurry can be  
15 removed to produce the predetermined three-dimensional pattern.

The present invention further includes a method for removing material from a workpiece. In one aspect, such a method can include the steps of providing a fixed abrasive tool as disclosed herein, and providing a workpiece to be treated. The fixed abrasive tool and workpiece can then be moved or rotated with respect to one another in order to polish a  
20 surface of the workpiece to produce a polished surface.

Typically, a polishing liquid can be introduced to the surface during the step of polishing in order to facilitate removal of debris. In one alternative aspect, the polishing liquid can be a moderate solvent for the organic matrix. In this way, the organic matrix can be slowly dissolved as exposed nanodiamond particles become worn in order to allow these  
25 particles to become dislodged and removed. As the organic matrix dissolves, new unused nanodiamond particles can be constantly exposed to maintain adequate material removal rates from the workpiece with an extended useful life. In yet another detailed aspect, the polished surface can have a surface roughness (Ra) less than about 2 nm, and preferably about 2 Å to about 10 Å.

The fixed abrasive tools of the present invention can be used to polish any number of workpieces. However, the present invention can be particularly suitable for polishing expensive workpieces such as silicon wafers, integrated circuitry, gemstones, and hard drive platters.

5           There has thus been outlined, rather broadly, the more important features of the invention so that the detailed description thereof that follows may be better understood, and so that the present contribution to the art may be better appreciated. Other features of the present invention will become clearer from the following detailed description of the invention, taken with the accompanying drawings and claims, or may be learned by the  
10       practice of the invention.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a cross-sectional view of one configuration for a fixed abrasive tool in accordance with the present invention.

15           FIG. 2 is a perspective view of a portion of a fixed abrasive tool surface showing frustoconical projections in accordance with an embodiment of the present invention.

FIG. 3 is a perspective view of a portion of a fixed abrasive tool surface showing pyramidal projections in accordance with an embodiment of the present invention.

FIG. 4 is a perspective view of a portion of a fixed abrasive tool surface showing  
20       frustopyramidal projections in accordance with an embodiment of the present invention.

FIG. 5 is a perspective view of a portion of a fixed abrasive tool surface showing cross projections in accordance with an embodiment of the present invention.

FIG. 6 is a perspective view of a portion of a fixed abrasive tool surface showing cylindrical projections in accordance with an embodiment of the present invention.

25           FIG. 7 is a perspective view of a portion of a fixed abrasive tool surface showing projections having a square cross-section in accordance with an embodiment of the present invention.

FIG. 8 is a perspective view of a portion of a fixed abrasive tool surface showing projections having a hexagonal cross-section in accordance with an embodiment of the  
30       present invention.

FIG. 9 is a perspective view of a portion of a fixed abrasive tool surface showing projections having a mixture of cross-sectional shapes in accordance with an embodiment of the present invention.

FIG. 10 is a perspective view of a portion of a fixed abrasive tool surface showing  
5 ridge projections having triangular prism shapes in accordance with an embodiment of the present invention.

FIG. 11 is a perspective view of a fixed abrasive tool showing projections having concentric rectangular arcuate ridges in accordance with an embodiment of the present invention.

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### **DETAILED DESCRIPTION**

Before the present invention is disclosed and described, it is to be understood that this invention is not limited to the particular structures, process steps, or materials disclosed herein, but is extended to equivalents thereof as would be recognized by those ordinarily  
15 skilled in the relevant arts. It should also be understood that terminology employed herein is used for the purpose of describing particular embodiments only and is not intended to be limiting.

It must be noted that, as used in this specification and the appended claims, the singular forms “a,” and “the” include plural referents unless the context clearly dictates  
20 otherwise. Thus, for example, reference to “a nanodiamond particle” includes one or more of such particles, reference to “a projection” includes reference to one or more of such structures, and reference to “a printing process” includes reference to one or more of such processes.

### **Definitions**

25 In describing and claiming the present invention, the following terminology will be used in accordance with the definitions set forth below.

As used herein, “fixed abrasive tool” and “fixed abrasive polishing tool” may be used interchangeably and refer to a polishing tool, e.g., chemical mechanical polishing or planarization pad, which has a plurality of projections formed thereon, and has plurality of  
30 nanodiamond particles embedded therein, or otherwise attached thereto. Configurations for

a number of traditional fixed abrasive tools such as fixed abrasive pads are well-known in the art including the pads described in the references enumerated in the background section above.

As used herein, “projection” refers to any structure which by design, is raised or protrudes above the working surface of a fixed abrasive tool. Projections useful in the present invention may take a wide variety of geometric configurations, including without limitation, cylinders, columns, bumps, mounds, pyramids, spikes, cubes, cones, etc. and may be arranged in a variety of patterns as discussed in more detail below.

As used herein with respect to projections, “height” refers to the distance between a distal point of a projection and a proximal point of a projection with respect to an underlying substrate.

As used herein, “loading ratio” refers to the amount of surface which is covered by projections and may vary depending on the application.

As used herein, “nanodiamond” refers to carbonaceous particles having crystal sizes in the nanometer range, i.e. about 1 nm to about 20 nm. Nanodiamond particles can also have nanometer range crystalline formations, e.g., about 1 nm to about 10 nm. Further, nanodiamond is intended to refer to particles having nanometer scale crystal structure. Nanodiamond particles can be formed using a number of known techniques. One nanodiamond formation technique involves the explosion of dynamite or other explosives to produce nanodiamond having nanocrystalline structure and has particle sizes in the range of from about 2 to about 10 nm. Typical fine diamond particles have a particle size larger than about 0.1  $\mu\text{m}$ . These diamond particles are most commonly produced by pulverizing larger diamond particles. This pulverization process results in particles having irregular shapes and sharp corners. Additionally, some diamond particles can be pulverized to form particles in the nanometer size range. However, these pulverized diamond particles are often not suitable for polishing materials which require a mirror finish and very low surface roughness, i.e. in the angstrom range. Further, diamond is significantly harder than most other common abrasives. For example, diamond typically has a Moh’s hardness (original scale) of about 10 or greater.

As used herein, “crystal” is to be distinguished from “particle.” Specifically, a crystal refers to a structure in which the repeated or orderly arrangement of atoms in a crystal lattice extends uninterrupted, although defects may be present. Many crystalline solids are composed of a collection of multiple crystals or grains. A particle can be formed  
5 of a single crystal or from multiple crystals as individual crystals grow sufficient that adjacent crystals impinge on one another to form grain boundaries between crystals. Thus, each crystal within a polycrystalline particle can have a random orientation.

As used herein, “carbonaceous coating” refers to a coating of non-diamond, carbon-containing materials. Typical carbon-containing materials can include amorphous carbon;  
10 fullerenes, e.g., C<sub>32</sub>, C<sub>60</sub>, C<sub>70</sub>, C<sub>76</sub>, C<sub>84</sub>, C<sub>90</sub> and C<sub>94</sub>; carbon onions, i.e. nested fullerenes, carbon nanotubes, diamond-like carbon, organic residual compounds, and the like.

As used herein, “amorphous diamond” and “diamond-like carbon” may be used interchangeably and refer to a material having carbon atoms as the majority element, with a  
15 substantial amount of such carbon atoms bonded in distorted tetrahedral coordination.

As used herein, “distorted tetrahedral coordination” refers to a tetrahedral bonding configuration of carbon atoms that is irregular, or has deviated from the normal tetrahedron configuration of diamond. Such distortion generally results in lengthening of some bonds and shortening of others, as well as the variation of the bond angles between the bonds.  
20 Additionally, the distortion of the tetrahedron alters the characteristics and properties of the carbon to effectively lie between the characteristics of carbon bonded in sp<sup>3</sup> configuration (i.e. diamond) and carbon bonded in sp<sup>2</sup> configuration (i.e. graphite). One example of material having carbon atoms bonded in distorted tetrahedral bonding is amorphous diamond and nanodiamond.

25 As used herein, “metallic” refers to a metal, or an alloy of two or more metals. A wide variety of metallic materials are known to those skilled in the art, such as aluminum, copper, chromium, iron, steel, stainless steel, titanium, tungsten, zinc, zirconium, molybdenum, etc., including alloys and compounds thereof.

As used herein, “ceramic” refers to a hard, often crystalline, substantially heat and  
30 corrosion resistant material which may be made by firing a non-metallic material,



sometimes with a metallic material. A number of oxide, nitride, and carbide materials considered to be ceramic are well-known in the art, including without limitation, aluminum oxides, silicon oxides, boron nitrides, silicon nitrides, silicon carbides, tungsten carbides, etc.

5           As used herein, “carbonaceous” refers to a material made substantially from carbon. A variety of carbonaceous materials and methods for the production thereof are known to those skilled in the art, including without limitation, diamond, nanodiamond, polycrystalline diamond, and diamond-like carbon.

10           As used herein, “moderate solvent” refers to an agent which slowly dissolves or removes the organic matrix. The rate of removal can vary depending on the loading ratio, polishing pressure, organic matrix, and the polishing liquid composition. A moderate solvent can dissolve the organic matrix at a rate sufficient to expose new nanodiamond particles without also releasing substantially unworn nanodiamond particles.

15           As used herein, “interface surface” refers to the surface of a mold, or ephemeral mold, upon which materials used in the fabrication of a predetermined three-dimensional pattern of a fixed abrasive tool are deposited.

          As used herein, “working surface” refers to the surface of a tool, which faces toward a workpiece, or performs a friction-involved function during a work process.

20           Concentrations, amounts, and other numerical data may be expressed or presented herein in a range format. It is to be understood that such a range format is used merely for convenience and brevity and thus should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited.

25           As an illustration, a numerical range of “about 1 micrometer to about 5 micrometers” should be interpreted to include not only the explicitly recited values of about 1 micrometer to about 5 micrometers, but also include individual values and sub-ranges within the indicated range. Thus, included in this numerical range are individual values such as 2, 3, and 4 and sub-ranges such as from 1-3, from 2-4, and from 3-5, etc.

This same principle applies to ranges reciting only one numerical value. Furthermore, such an interpretation should apply regardless of the breadth of the range or the characteristics being described.

### **Invention**

5 Referring now to FIG. 1, a fixed abrasive tool 10 in accordance with the present invention is shown. The fixed abrasive tool can include a substrate 12 having a polishing layer 14 attached to the substrate. In accordance with the present invention, the polishing layer can include an organic matrix with nanodiamond particles therein.

10 The polishing layer 14 can be provided in a number of configurations. In some embodiments of the present invention, the polishing layer can be discontinuous as shown in FIG.1. However, the polishing layer can also be continuous. Most typically, the polishing layer can be formed in a predetermined three-dimensional pattern. In this way, the polishing properties, contact surface, loading ratio, debris removal, and the like can be designed for a specific application. Thus, in one embodiment, the polishing layer can be  
15 formed as a substantially flat layer. However, most often, the predetermined three-dimensional pattern can include a plurality of projections 16. As can be seen, by a comparison of FIGs. 2 through 11, the specific geometric shape of the projections can vary considerably. Further, the specific pattern in which the projections are formed, their exact size, and the concentration of projections on a substrate can also be varied. Suitable  
20 projections can depend largely on the particular polishing environment; however, generally the projections can be in the form of spaced projections, shaped channels, and the like. Specific non-limiting examples of suitable projections include conical, frustoconical, pyramidal, frustopyramidal, cubic, parallelepiped, rectangular, cross, cylindrical, column, ridge, and combinations thereof. FIGs. 2 through 6 illustrate several suitable projection  
25 configurations. In one aspect, the projections can have a frustoconical shape. In another aspect, the projections can have a frustopyramidal shape. In yet another aspect, the projections can be a column. In another aspect, the projections can be a series of parallel ridges. Additionally, the projections can be rounded mounds, hemispheric, or grid pattern ridges.

In some embodiments, the projections can be columns having a cross-sectional area, taken in a plane parallel with the substrate surface, which is a circle, ellipse, triangle, square, rectangle, pentagon, hexagon, heptagon, octagon, and combinations of these shapes such as those shown in FIGs. 6 through 9. Thus, sides of the projections can be perpendicular to the substrate surface as in FIGs. 1 and 6 through 9, or can be tapered as shown in FIGs. 2 through 4. In other embodiments, the projections can be in the form of ridges which have a variety of configurations. For example, the ridges can be rectangular, prismatic, and the like. FIG. 10 illustrates a three-dimensional pattern of parallel triangular prisms. Additionally, FIG. 11 illustrates one specific configuration for a fixed abrasive polishing pad in accordance with the present invention. FIG. 11 shows concentric arcuate rectangular ridges having arcuate and radial trenches therebetween to facilitate debris removal. Each of the above-listed projection configurations may achieve a different result or be more or less useful with various fixed abrasive tools.

The projections can be placed in a predetermined pattern which may be random, evenly spaced, or varied spacing to produce varying rates of polishing across a workpiece. In one aspect, the projections can have a predetermined pattern which is a regular grid pattern, offset rows, spiral pattern, or regions of differing patterns and/or concentration of projections. Further, each projection can be uniformly oriented or rotated with respect to neighboring projections. In this way, polishing artifacts such as skids, pits, and the like can be reduced. The predetermined pattern of projections can be designed based on a wide variety of factors. For example, among these factors are the desired loading ratio and debris removal. In one aspect, the projections can be formed such that the fixed abrasive tool has a loading ratio of from about 0.05 to about 0.5, and preferably from about 0.1 to about 0.3.

Generally, each projection (sometimes referred to as a pole) has a diameter from about 100  $\mu\text{m}$  to about 300  $\mu\text{m}$  and a height from about 10  $\mu\text{m}$  to about 80  $\mu\text{m}$ . Typically, the projections can have a diameter of about 200  $\mu\text{m}$ , and a height of about 30-50  $\mu\text{m}$ . However, specific dimensions can vary somewhat depending on the particular needs of a specific polishing application. Additionally, while certain configurations may call for projections of different heights on a single tool, in yet an additional aspect of the invention, the projections may have a uniform height. In an additional embodiment of the present

invention, the projections can have a height from 20  $\mu\text{m}$  to about 300  $\mu\text{m}$  and a diameter from about 10  $\mu\text{m}$  to about 300  $\mu\text{m}$ . As a general matter, it can be desirable to increase the surface area of each projection, in order to minimize the number of nanodiamond particles in internal portions of the projections. Although many nanodiamond particles originally in  
5 internal portions will become exposed during use, a configuration which leaves a substantial number of unused nanodiamond particles at the end of the useful life of a tool is undesirable.

Parameters, such as spacing between the projections, the overall pattern in which the projections are arranged, and the total number or density of projections on the fixed  
10 abrasive tool can all be varied. However, in one aspect, the projections are spaced apart for a distance of less than about 150  $\mu\text{m}$ . In another aspect, the projections are spaced apart for a distance of less than about 100  $\mu\text{m}$ . In yet a further aspect, the projections are spaced apart for a distance of less than about 50  $\mu\text{m}$ . In another aspect of the invention, the projections may be uniformly spaced apart.

15 Further, with reference to FIG. 1, the polishing layer 14 can include nanodiamond particles dispersed in an organic matrix. Suitable nanodiamond particles can have a particle size which is sufficiently small so as to polish a workpiece to produce a very low surface roughness. Thus, suitable particle sizes can depend on the desired surface roughness. As a general guideline, the nanodiamond particles can have a particle size from about 1 nm to  
20 about 20 nm, and preferably from about 2 nm to about 10 nm. In cases where extremely smooth surfaces are desired, a preferred nanodiamond particle size can be from about 3 nm to less than 10 nm, and most preferred from about 4 nm to about 6 nm. Suitable nanodiamond particles can also be substantially free of sharp edges. Preferably, nanodiamond particles can be substantially rounded with substantially no sharp corners or  
25 irregular protrusions.

One currently preferred source of nanodiamond particles is from explosion synthesis. These nanodiamond particles can be produced by explosion of explosives such as, but not limited to, trinitrotoluene (TNT), trinitrotriazacyclohexane (RDX, i.e. research department explosive hexogen), HMX, PETN, BTF, HNX, PBX, picrite, trinitrophenolo  
30 picric acid (TNP), trinitroresorcin (TNR), tritonal, BRX, other known explosive charges,

and mixtures thereof. Although the specific explosion conditions can vary depending on the specific process used, such explosion synthesis processes can achieve temperatures around 3000 °C and pressures of up to 12 GPa. These nanodiamond particles are not produced by pulverizing or milling larger particles. Without being bound to any particular theory, it appears that nanodiamond particles formed by explosion synthesis are formed *in situ* via crystallization of a liquid solution of diamond. Due to the extremely short synthesis time and conditions, these types of nanodiamond particles typically have a diamond-like carbon core surrounded by amorphous carbon, concentric fullerenes, i.e. carbon onions, and other carbon and non-carbon residual materials. Additionally, explosion synthesis nanodiamond particles include a high content of defects. These defects are on a sub-nanoscale and tend to allow the nanodiamond particles to cleave and chip along these sub-nanoscale defects during use. Thus, as the nanodiamond particles become worn, the particles can chip and break to expose sub-nanoscale cutting surfaces. As a result, these nanodiamond particles do not slide along the surface of a workpiece, but rather cut and remove material on a sub-nanoscale. Thus, in one preferred aspect of the present invention, the nanodiamond particles can be grown *in situ* as nanodiamond through explosion synthesis, rather than pulverized from larger diamond particles.

Nanodiamond concentration within the polishing layer can also vary depending on the intended application. Typically, the polishing layer can have a nanodiamond concentration from about 5 vol% to about 60 vol%, and preferably from about 10 vol% to about 30 vol%. Further, suitable nanodiamond particles can have a Moh's hardness of about 9.5 or greater, and preferably 10 or greater.

In one alternative embodiment of the present invention, the nanodiamond particles include a carbonaceous coating. The carbonaceous coating can typically have a thickness from about 0.5 nm to about 5 nm, and typically about 1 nm to 2 nm. This coating provides a soft skin with lubricating properties, and a superhard interior suitable for polishing a surface. Thus, material can be removed from a workpiece without scratching or damaging the workpiece. As a result, extremely smooth surfaces can be produced using coated nanodiamond particles. For example, in some cases a polished surface can have a surface roughness (Ra) of less than about 2 nm, and preferably from about 2 Å to about 10 Å.

When using nanodiamond particles in accordance with the present invention, Ra values of from about 2 Å to about 9 Å can also be achieved.

The polishing layer includes an organic matrix as a binder for the nanodiamond particles. Various materials can be used in connection with this purpose. Organic matrix material can be thermoplastic or thermosetting materials. Such organic binders can be solidified by curing, drying, or cooling. Curable organic matrix materials are particularly suitable and can be cured by a number of known mechanisms such as ultraviolet light, visible light, electron-beam, secondary reagent, or other energy sources. Several non-limiting examples of suitable organic matrix materials include epoxy, polyimide, polyethylene terephthalate (MYLAR), polytetrafluoroethylene (TEFLON), polyurethane, polycarbonate, polyester, and mixtures thereof. These organic matrix materials are currently preferred; however, other organic matrix materials can be used such as, but not limited to, phenolics, acrylates, amino resins such as urea-formaldehydes and melamine-formaldehydes, aminoplast resins, alkyd resins, phenolic-latex resins, latex resins, epoxy resins such as bisphenols, isocyanates, isocyanurates, polysiloxane resins, acrylated epoxy resins, ceramers, and the like. In one specific aspect, the organic matrix can be an epoxy. In another aspect, the organic matrix can be polyurethane. Typical organic binders can be polymerized using any number of polymerization techniques such as condensation polymerization, addition polymerization, free radical polymerization, emulsion polymerization, and the like. The exact quantities of organic binder can depend largely on the specific material used. Typically, the organic binder can comprise from about 10 wt% to about 95 wt% of the slurry, and in some cases from about 30 vol% to about 95 vol%.

Alternatively, an additional solvent or other liquid can be added to the slurry in order to facilitate processing and formation of the polishing layer. Suitable solvents can include, but are not limited to, water, alcohols, hydroxides, and the like. The quantity of solvent can vary depending on the formation process; however, as a general guideline, any additional solvent can comprise from about 5 wt% to about 30 wt% of the slurry. Additionally, the amount of solvent can depend on the process used to form the polishing layer. For example, if screen printing is used, the desired viscosity can range from about 50

cps to about 10,000 cps. When screen printing, the solvent can comprise from about 10 wt% to about 20 wt% of the slurry.

Due to the small particle sizes of the nanodiamond particles used in the present invention, the nanodiamond particles can tend to agglomerate. Dispersants can be added to the slurry in order to reduce or prevent agglomeration of nanodiamond particles. Several non-limiting examples of dispersants include anionic surfactants, electrolytes, alcohols, metal chlorides and nitrates such as Al, Na, Ca, and Fe chlorides and nitrates, and the like. Other suitable nanodiamond dispersants include isopropyl triisosteroyl titanate, polyethylene-oxides, and the like.

Optionally, the slurry can further comprise filler materials such as, but not limited to, polymeric particles, silicates, carbonates, talc, and other relatively soft materials. Specific non-limiting examples of filler materials include graphite, silica glass, clay, feldspar, mica, metal sulfates, gypsum, wood flour, carbon black, metal oxides, thermoplastic particles such as polycarbonate, polyetherimide, polyester, polyethylene, polysulfone, polystyrene, acrylonitrile-butadiene-styrene block copolymer, polypropylene, acetal polymers, polyurethanes, nylon particles; thermosetting particles such as phenolic bubbles, phenolic beads, polyurethane foam particles, phenolic resins, urethane resins, epoxy resins, melamine-formaldehyde, acrylate resins, acrylated isocyanurate resins, urea-formaldehyde resins, isocyanurate resins, acrylated urethane resins, acrylated epoxy resins, and the like; metal halide salts, metals such as lead, tin, cobalt, antimony, iron, and titanium; and the like. Typically, filler materials can be relatively soft, i.e. a Moh's hardness of less than about 6. In this way, the nanodiamond particles can provide the dominant material removal action from the workpiece. Although filler materials can be added, the slurry of the present invention is most often substantially free of abrasive particles having a Moh's hardness greater than about 6 to 7, exclusive of nanodiamond particles.

In an additional alternative embodiment, the organic matrix can be configured to affect the polishing properties of the fixed abrasive tool. For example, specific polymeric materials can be adjusted in hardness and degree of cross-linking in order to increase or decrease erosion of matrix material during polishing. In this way, the organic matrix

hardness can be adjusted to complement the polishing and hardness of the nanodiamond particles. Specifically, in some cases it can be desirable to allow nanodiamond particles at the surface to fall out after a predetermined time of polishing. Subsequently, the loose nanodiamond particles can become suspended in a polishing liquid to further polish the workpiece. Similarly, the slurry can further comprise a softening agent to adjust the rate of erosion of the organic matrix upon solidification. Non-limiting examples of suitable softening agents include phthalate esters, polyethylene glycol, polyvinyl chloride, dibutyl phthalate, alkyl benzyl phthalate, polyvinyl acetate, polyvinyl alcohol, cellulose esters, phthalate, silicone oils, adipate and sebacate esters, polyols, polyols derivatives, t-butylphenyl diphenyl phosphate, tricresyl phosphate, castor oil, and combinations thereof. If used, softening agents can comprise from about 20 wt% to about 70 wt% of the slurry.

In yet another additional embodiment, various intermediate materials can be provided in the slurry which forms chemical bonds between the diamond or carbonaceous coating and the organic matrix. For example, silanes, titanates, zircoaluminates, or other coupling agents can form chemical bonds with both diamond and typical polymeric materials. In this way, the nanodiamond particles can be retained in the organic matrix approximately until the nanodiamond particles at the surface are substantially worn or spent. When used, intermediate materials can comprise from about 1 wt% to about 25 wt% of the slurry.

Further, the slurry can comprise additives such as expanding agents, fibers, anti-static agents, initiators, suspending agents, lubricants, wetting agents, surfactants, pigments, dyes, UV stabilizers, complexing agents, chain transfer agents, accelerators, catalysts, and activators. Those skilled in the art are familiar with such additives and can determine appropriate conditions and quantities for incorporation of these additives based on desired slurry and tool properties.

The polishing layer 14 can be formed on any suitable substrate 12, as shown in FIG. 1. The substrate typically provides a mechanical support surface which can be attached to any number of tools or devices known to those skilled in the art. Those skilled in the art will recognize that various slurry compositions can provide components which adhere to or otherwise provide attachment of the polishing layer to the substrate, as discussed and



illustrated in the aforementioned references. Materials which are suitable for use as the substrate can include, but are not limited to, metals, polymers, and composites or alloys of these materials. Further, the substrate can be provided in the form of a solid plate, film, foil, fibrous woven material, paper, or the like. As a general matter, the substrate can be made from numerous materials which are sufficiently durable to impart a useful lifespan to the fixed abrasive tool including ceramic and metallic materials. In one aspect of the invention, the substrate can be made of an anti-corrosive material that is substantially impervious to degradation from the polishing liquid used in connection with the fixed abrasive tool. A variety of metallic and ceramic materials may have such qualities, such as stainless steel and corundum.

In one aspect, the substrate can comprise, be substantially made of, or consist of a polymeric material. Non-limiting examples of suitable polymeric materials include polyethylenes, terephthalates, polyesters, polyurethanes, polycarbonates, polyamides, polypropylenes, polyethylenes, polyimides, and the like.

In another aspect of the invention, the substrate can comprise, be substantially made of, or consist of a metallic material. Suitable metallic materials can include without limitation, metals such as, copper, titanium, tungsten, tantalum, nickel, zirconium, zinc, vanadium, chromium, steel, stainless steel, as well as alloys of these metals.

The substrate can additionally comprise, be substantially made of, or consist of a ceramic material. Nearly any ceramic material that sufficiently meets the hardness and durability requirement demanded of the abrasive tool can be used including various silicon containing materials. In one aspect, certain oxide, carbide, and nitride compounds may be used, including without limitation, silicon carbide, quartz, corundum or sapphire, silicon nitride, boron nitride (including cubic boron nitride), tungsten carbide, titanium carbide, and zirconium carbide, zinc oxide, zirconia, aluminum nitride, titanium nitride, and zirconium nitride, and mixtures or composites thereof. In one aspect, the ceramic material can be a silicon carbide. In another aspect, the ceramic material can be a cemented tungsten carbide.

The above-described fixed abrasive tools can be formed in accordance with at least one of several methods. The fixed abrasive tools of the present invention can be formed, in

one embodiment, by providing a suitable substrate. Frequently, it can be necessary to prepare the substrate prior to forming projections thereon. By way of example, in a case where the substrate is metallic, the surface can be machined using a well-known Computer Numerical Machine (CNC), or the surface can be prepared by using an Electrical Discharge Machine (EDM). Additionally, when the substrate is made of silicon or a silicon-containing material, the surface can be chemically prepared using conventional etching techniques, such as lithography. Such techniques are well-known to those of ordinary skill in the art, and various other techniques for preparing the surface that are not mentioned will be readily recognized by those of ordinary skill in the art.

Further, a slurry can be prepared which includes nanodiamond particles and an organic binder. The slurry can then be formed on the substrate in a predetermined three-dimensional pattern. The predetermined three-dimensional pattern can take a variety of forms, such as those discussed above. In one embodiment, the three-dimensional pattern can be formed by printing using techniques such as screen-printing, gravure, and the like. For example, in order to form three-dimensional patterns, a plurality of layers can be printed. Typically, a pattern of slurry can be printed on the substrate. Any excess solvent or liquid can then be driven off to at least partially harden the printed portions. This process can be repeated by printing adjacent layers either directly on one another or by stacking printed layers to form a three-dimensional pattern in order to achieve a desired projection height. Further, each layer can be printed with differing patterns such that projections can have a vertical profile, e.g., conical, pyramidal, etc. projections. Various shapes and configurations can be achieved using screen printing or other printing techniques which are known to those skilled in the printing arts.

The printed pattern of slurry can then be solidified to produce abrasive projections of nanodiamond particles dispersed in an organic matrix. Typically, the slurry can be solidified by curing using heat, ultraviolet light, or other energy source appropriate for a particular organic binder.

Alternatively, the predetermined three-dimensional pattern can be formed by tape casting a layer of slurry on a substrate. In one aspect, select portions of the tape cast layer can be removed to produce the predetermined three-dimensional pattern. For example,

select portions can be etched away chemically to leave a desired pattern of projections. Alternatively, portions of the tape cast layer which correspond to projections to be formed can be cured, e.g., using UV curable organic binder, while remaining portions are left uncured. The uncured portions can then be easily removed without removing or damaging the cured projections to form the predetermined three-dimensional pattern. The removed portions can be recycled for use in subsequent processing or otherwise disposed of. In one alternative, select portions of the organic binder can be cured or partially cured using conventional photolithography techniques.

In yet another alternative, the predetermined three-dimensional pattern can be formed using a substrate which includes an interface surface. The interface surface can have a plurality of concavities inversely matching a plurality of projections configured for forming the predetermined three-dimensional pattern. Thus, the substrate acts as a mold for forming the projections. In this case, the step of printing can include at least partially filling the plurality of concavities with the slurry. A backing material can then be placed on the exposed side of the printed slurry. In some cases, an adhesive or other resin can be used to join the backing material to the slurry. Upon solidifying and/or at least partially removing solvent from the slurry, the substrate can be removed. The substrate can be physically removed, i.e. using a polytetrafluoroethylene mold as the substrate, or chemically dissolved with a strong acid or appropriate solvent. The backing material can then act as a substrate for formation of a fixed abrasive tool in accordance with known principles. A wide variety of suitable materials for attaching the backing layer to form a tool will be readily recognized by those of ordinary skill in the art, such as brazing, adhesives, etc.

A wide variety of fixed abrasive tools can be formed in accordance with the principles of the present invention. Non-limiting examples of fixed abrasive tools can include CMP polishing pads, polishing belts, indexable polishing rolls, and the like.

The fixed abrasive tools of the present invention can be used to polish a wide variety of workpieces. Several specific examples of suitable workpieces include silicon wafers, integrated circuitry, gemstones, hard drive platters, magnetic heads, and the like. In one preferred embodiment, the workpiece can be a silicon wafer. Other workpieces can include gallium arsenide wafers or any silicon wafers having various features thereon, e.g., doped

regions, epitaxial layers, ceramic layers, device features, etc. However, as a general matter, the fixed abrasive tools of the present invention can be used to polish other workpieces such as, but not limited to, ceramic, stone, polymer, glass, metal, and composites or alloys thereof. The workpiece can be polished by contacting the fixed abrasive polishing pad to the workpiece and applying pressure and relative motion between the surface and the fixed abrasive polishing pad sufficient to remove material from the surface to produce a polished surface. Using the nanodiamond fixed abrasive tools of the present invention, pressure can be applied during polishing at from about 1 psi to about 100 psi, and in some aspects can range between 10 psi and 20 psi. Generally, at this range of pressures, polishing removes material from the polished surface at a rate from about 10 Å/min to about 1000 Å/min, and preferably from about 100 Å/min to about 500 Å/min, and most preferably from about 150 Å/min to about 450 Å/min. Faster rates of removal can tend to cause damage of the workpiece and/or undesirable microcracks.

In one detailed aspect of the present invention, a polishing liquid can be introduced to the surface of the workpiece during polishing. Any number of liquids can be used such as, but not limited to, water, acids, alcohols, and the like. Those skilled in the art can choose a polishing liquid based on the type of substrate. For example, when polishing silicon wafers or oxide-containing layers a hydroxide or other basic liquid can be used. Preferably, the polishing liquid can be substantially free of abrasive particles upon introduction to the surface. The polishing liquid acts to carry away material and debris removed from the workpiece. This helps to prevent excessive buildup or glazing which reduces the useful life of the fixed abrasive tool. Similarly, the polishing liquid can be chosen to chemically react with the workpiece to facilitate the removal and polishing action of the fixed abrasive tool.

In one alternative embodiment, the polishing liquid can be a moderate solvent for the organic matrix. Examples of suitable moderate solvents will depend on the organic matrix; however, several non-limiting examples include acetone, moderate to weak acids, toluene, trichloroethane, surfactants, dilute sodium hydroxide, potassium hydroxide, and the like. Thus, during polishing the organic matrix can slowly be removed to expose fresh and unused nanodiamond particles. Further, the rate of removal of the organic matrix is

typically higher at high pressure points of contact between the fixed abrasive tool and the workpiece. In some embodiments, the organic matrix and polishing liquid are chosen such that the polishing layer dissolves at points of contact at a rate from about 1 Å/min to about 100 Å/min, and in some embodiments from about 2 Å /min to about 50 Å/min.

5           Of course, it is to be understood that the above-described arrangements are only illustrative of the application of the principles of the present invention. Numerous modifications and alternative arrangements may be devised by those skilled in the art without departing from the spirit and scope of the present invention and the appended claims are intended to cover such modifications and arrangements. Thus, while the present  
10 invention has been described above with particularity and detail in connection with what is presently deemed to be the most practical and preferred embodiments of the invention, it will be apparent to those of ordinary skill in the art that numerous modifications, including, but not limited to, variations in size, materials, shape, form, function and manner of operation, assembly and use may be made without departing from the principles and  
15 concepts set forth herein.